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(54) Title: AQUEOUS COATING MATERIAL AND MODULAR SYSTEM FOR PRODUCING SAME
Wässriger Beschichtungsstoff und Modulsystem zu seiner Herstellung

(57) Abstract

The invention relates to an aqueous coating material which can be prepared by combining (A) at least one base paint which contains (a1) at least one binding agent which optionally can be dissolved or dispersed in water, (a2) at least one color- and/or effect-imparting pigment, and (a3) at least one organic solvent miscible with water; and which base paint optionally contains (a4) water, (a5) at least one crosslinking agent, and/or (a5) at least one auxiliary and/or additive; (B) at least one solid, fine-particle mixed coating composition containing (b1) at least one fine-particle solid binding agent, which can be dissolved or dispersed in water; and (C) an aqueous medium. The invention also relates to a modular system for producing aqueous coating materials containing (I) at least one color- and/or effect-imparting module containing at least one base paint (A), (II) at least one solids module containing at least one fine-particle solid, mixed coating composition (B), and (III) at least one dispersion module containing an aqueous medium (C).

Aqueous Coating Material and Modular System for Producing Same

The present invention relates to novel aqueous coating materials, which contain at least one base paint (A), at least one mixed coating composition (B), and an aqueous medium (C). Furthermore, the present invention relates to a novel modular system, which is used for preparing the novel aqueous coating materials. Not least, the present invention relates to a novel process for the preparation of coating materials.

Aqueous coating materials of the aforementioned type, in which the mixed coating composition (B) and the aqueous medium (C) are mixed with one another, and the appropriate modular system based on anionically or nonionically stabilized dispersions, which have a color module and/or effect module and a mixed coating composition module, are known from the patents EP-A 0 578 645 and EP-A 0 698 773. The mixed coating composition (B) thereof or the mixed coating composition module thereof contains binders dissolved or dispersed in water. Modular systems based on cationically stabilized dispersions are known from the patent DE-A 44 15 292.

The prior-art aqueous coating materials can be prepared with the use of known modular systems in a simple manner in a multitude of shades, optionally associated with very different optical effects, such as metallic effects, pearlescent effects, or angle-dependent effects. The modular systems, for this reason, were particularly able to succeed in automotive refinishing and hereby exhibit numerous other advantages. Thus, they have a comparatively low solvent content and are easy to apply and to dispose of. The coatings prepared therefrom exhibit a property profile, which totally meets the high demands of the market, relative to optical properties, hardness, flexibility, scratch resistance, solvent resistance, and weather resistance.

These known coating materials and the mixed coating composition module of the prior-art modular systems contain binders, which are dissolved or dispersed in water and are attacked and destroyed by microorganisms in the dissolved or dispersed state, particularly during prolonged storage; as a result, these systems of coating materials and mixed coating composition modules become unusable and must be discarded, which is a serious disadvantage from the technical and economic standpoint.

If the affected coating materials and mixed coating composition modules are nevertheless used, they afford coatings that no longer meet the user's requirements, particularly in the automotive industry.

Efforts were therefore made to overcome these problems by addition of bactericidal and/or fungicidal substances, but the old problems are traded for new ones. In one respect, the user and environment are more intensely exposed to these toxic substances, which in itself is a disadvantage. Moreover, with the widespread and active use of these substances, resistance can develop in microorganisms, the harmful actions of which are not limited to the technical field under discussion but also extend to other fields.

Powdered, redispersible binders, which are processed with solid components, typical for coatings, into powdered coating materials, are known from the German patent DE-A 44 07 841. The ready-to-use coating materials can be prepared from the dry mixtures by combination with water. Use in modular systems as solid, fine-particle mixed coating compositions has not been described, however.

The object of the present invention is to find a novel coating material that does not have the aforementioned disadvantages and is attacked to a much lower extent or not at all by microorganisms, and therefore has a higher storage stability than prior-art coating materials, whereby the advantageous properties thereof are at least retained, if not even further improved.

Accordingly, the novel coating material was found, which is prepared by combining

(A) at least one base paint, containing

- (a1) at least one binder, optionally soluble or dispersible in water,
- (a2) at least one color- and/or effect-imparting pigment, and
- (a3) at least one water-miscible organic solvent, and if desired containing
- (a4) water,
- (a5) at least one crosslinking agent, and/or

(a6) at least one auxiliary and/or additive;

(B) at least one solid, fine-particle mixed coating composition, containing

(b1) at least one fine-particle solid binder, soluble or dispersible in water;

and

(C) an aqueous medium.

In the text that follows, the novel coating material will be designated as "the coating material of the invention."

In addition, the novel modular system was found for the preparation of aqueous coating materials, containing

(I) at least one color and/or effect module, containing

(A) at least a base paint, containing

(a1) at least one binder, optionally soluble or dispersible in water,
(a2) at least one color- and/or effect-imparting pigment, and
(a3) at least one water-miscible organic solvent, and if desired containing
[(a4) water,]
(a5) at least one crosslinking agent, and/or
(a6) at least one auxiliary and/or additive;

(II) at least one solids module, containing

(B) at least one fine-particle solid mixed coating composition, containing

(b1) at least one fine-particle solid binder, soluble or dispersible in water;

and

(III) at least one dispersion module, containing

(C) an aqueous medium.

In the text that follows, the novel modular system for the preparation of the coating material of the invention will be designated as the "modular system of the invention" for the sake of brevity.

Not least, a novel process was found for the preparation of an aqueous coating material, in which

(A) at least one base paint, containing

(a1) at least one binder, optionally soluble or dispersible in water,
(a2) at least one color- and/or effect-imparting pigment, and
(a3) at least one water-miscible organic solvent,
and if desired containing
(a4) water,
(a5) at least one crosslinking agent, and/or
(a6) at least one auxiliary and/or additive;

and

(B) at least one mixed coating composition

are dispersed in

(C) an aqueous medium

and which is characterized in that the mixed coating composition (B) is fine-particle and solid and contains at least one fine-particle solid binder (b1), or consists thereof.

In the text that follows, the novel process for the preparation of a coating material will be designated as the "process of the invention" for the sake of brevity.

The present invention also relates to the use of the coating materials of the invention, the modular system of the invention, and the process of the invention in production-line automotive finishing, refinishing, and the coating of plastics, particularly with topcoats or fillers.

The particular advantage of the coating material of the invention and the modular system is that the mixed coating composition (B) or the solids module (II) is substantially free of dissolved or dispersed binders (b1), so that even with prolonged storage they are no longer attacked by microorganisms or attacked only to an extent that does not perceptibly harm their application properties. On the other hand, the particular advantage of the coating material of the invention and the modular system is that the mixed coating composition (B) and the solids module (II) can be stored for an especially long period, without their application properties being affected. Furthermore, as fine-particle solids, they can be metered especially simply, rapidly, and precisely within the scope of the process of the invention into the base paint (A) and into the aqueous medium (C) or into the color and/or effect module (I) and into the dispersion module (III).

It is moreover surprising that the coating material of the invention can be prepared by simple mixing, without the need for costly apparatus for mixing or dispersing, as are described, for example, in the German patent DE-A 195 10 651. The coating material of the invention is therefore particularly also suitable for the field of automotive refinishing, because it can be prepared by the painter immediately before its application by simple mixing of modules (I), (II), and (III).

It is advantageous, in addition, that the coating material of the invention has a comparatively low content of volatile organic solvents, although it is prepared with the use of organically dissolved or dispersed binders (a1).

Moreover, the coating agents of the invention assure a high variability, because not only the crosslinking agents, pigments, and auxiliaries and additives, recommended for aqueous coating agents, but also those employed in conventional systems can be used.

The component, essential to the invention, of the coating material of the invention is a fine-

particle solid mixed coating composition (B). As taught by the invention, said coating composition contains at least one fine-particle solid binder (b1), soluble or dispersible in water.

The component, essential to the invention, of the modular system of the invention is again a solids module (II). As taught by the invention, said module contains at least one fine-particle solid mixed coating composition (B), the essential component of which is at least one fine-particle solid binder (b1), soluble or dispersible in water.

Within the scope of the present invention, the term "module" designates a standardized, ready-to-use commercial product, the application property profile of which is precisely matched to the property profiles of other modules and supplements these, so that the modules together can be combined into a modular system.

The fine-particle solid binders (b1), soluble or dispersible in water, to be used as taught by the invention, are oligomeric or polymeric resins. The binders (b1) are physically drying or they contain functional groups, which may react with the crosslinking agents (a5) or (b3) described below.

Examples of suitable functional groups are amino, thio, carbonate, epoxide, and/or hydroxyl groups, of which hydroxyl groups are especially advantageous and therefore especially preferred according to the invention.

Thus, the fine-particle solid binders (b1) preferred according to the invention are hydroxyl group-containing oligomeric or polymeric resins.

Examples of fine-particle solid binders (b1) preferred according to the invention are hydroxyl group-containing linear and/or branched and/or block-like, comb-like, and/or randomly structured poly(meth)acrylates, or acrylate copolymers, polyesters, alkyds, aminoplasts, polyurethanes, acrylated polyurethanes, acrylated polyesters, polylactones, polycarbonates, polyethers, epoxy resin–amine adducts, (meth)acrylate diols, partially saponified polyvinyl esters, or polureas, of which the acrylate copolymers, the polyesters, the polyurethanes, the polyethers, and the epoxy resin–amine adducts are especially advantageous and for this reason, used especially preferably.

In regard to the producibility, handling, and the especially advantageous properties of the coating agents of the invention prepared herewith, the acrylate copolymers, the polyesters, and/or the polyurethanes, but particularly the polyurethanes offer very special advantages, for which reason they are used very especially preferably as taught by the invention.

According to the invention, the fine-particle solid binders (b1) by themselves are soluble or dispersible in water.

Examples of suitable water-soluble or -dispersible, fine-particle solid binders (b1) contain either

(i) functional groups, which can be converted into cations by neutralizing agents and/or quaternization agents, and/or cationic groups

or

(ii) functional groups, which can be converted into anions by neutralizing agents, and/or anionic groups

and/or

(iii) nonionic hydrophilic groups.

Examples of suitable functional groups (i), to be used as taught by the invention, which can be converted into cations by neutralizing agents and/or quaternization agents, are primary, secondary, or tertiary amino groups, secondary sulfide groups, or tertiary phosphine groups, particularly tertiary amino groups or secondary sulfide groups.

Examples of suitable cationic groups (i), to be used as taught by the invention, are primary, secondary, tertiary, or quaternary ammonium groups, tertiary sulfonium groups, or quaternary phosphonium groups, preferably quaternary ammonium groups, or quaternary ammonium groups, tertiary sulfonium groups, but especially tertiary sulfonium groups.

Examples of suitable functional groups (ii), to be used as taught by the invention, which can be converted into anions by neutralizing agents, are carboxylic acid groups, sulfonic acid groups, or phosphonic acid groups, particularly carboxylic acid groups.

Examples of suitable anionic groups (ii), to be used as taught by the invention, are carboxylate groups, sulfonate groups, or phosphonate groups, particularly carboxylate groups.

Examples of suitable nonionic hydrophilic groups (iii), to be used as taught by the invention, are

polyether groups, particularly poly(alkylene ether) groups.

The selection of groups (i) or (ii) is to be made such that no interfering reactions with the functional groups, which may react with the crosslinking agents (b3), are possible. One skilled in the art can therefore make the selection in a simple manner based on his know-how.

Examples of suitable neutralizing agents for functional groups (i) convertible into cations are inorganic and organic acids, such as sulfuric acid, hydrochloric acid, phosphoric acid, formic acid, acetic acid, lactic acid, dimethylolpropionic acid, or citric acid.

Examples of suitable neutralizing agents for functional groups (ii) convertible into anions are ammonia, ammonium salts, such as, for example, ammonium carbonate or ammonium hydrogen carbonate, as well as amines, such as, e.g., trimethylamine, triethylamine, tributylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, diethylethanolamine, methyldiethanolamine, triethanolamine, and the like. The neutralization can occur in the organic phase or in the aqueous phase. Dimethylethanolamine is used preferably as the neutralizing agent.

In general, the amount of neutralizing agent is selected such that 1 to 100 equivalents, preferably 50 to 90 equivalents of the functional groups (i) or (ii) of the binder (b1) are neutralized.

In regard to producibility, handling, and the especially advantageous properties of the coating materials and modular systems of the invention, prepared herewith, the fine-particle solid binders (b1), which contain the anion-forming groups and/or anions (ii), particularly the carboxylic acid groups and/or carboxylate groups, offer very special advantages, which is why they are used very especially preferably as taught by the invention.

Examples of very especially preferred fine-particle solid binders (b1), to be used as taught by the invention, of the last mentioned type are:

(b11) acrylate copolymers (b1) described below, containing hydroxyl groups and carboxylic acid groups and/or carboxylate groups,

(b12) the polyester resins (b1) described below, containing hydroxyl groups and carboxylic acid groups and/or carboxylate groups, and/or

(b13) the polyurethane resins (b1) described below, containing hydroxyl groups and carboxylic acid groups and/or carboxylate groups.

Fine-particle solid acrylate copolymers (b11) are used especially, which can be obtained in the presence of at least one polymerization initiator by polymerization in bulk, solution polymerization in an organic solvent or a solvent mixture, by emulsion polymerization, or precipitation polymerization in water of

m1) a substantially acid group-free (meth)acrylic acid ester, different from (m2), (m3), (m4), (m5), and (m6) and copolymerizable with (m2), (m3), (m4), (m5) and (m6), or a mixture of such monomers,

m2) an ethylenically unsaturated monomer, copolymerizable with (m1), (m3), (m4), (m5), and (m6) and different from (m5), which carries at least one hydroxyl group per molecule and is substantially free of acid groups, or a mixture of such monomers,

m3) an ethylenically unsaturated monomer, carrying at least one acid group, which can be converted into the corresponding acidic anion group per molecule and copolymerizable with (m1), (m2), (m4), (m5), and (m6), or a mixture of such monomers, and

m4) if desired, one or more vinyl esters of monocarboxylic acids, branched at the alpha position, having 5 to 18 C atoms per molecule, and/or

m5) if desired, at least one reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of a monocarboxylic acid, branched at the alpha position, having 5 to 18 C atoms per molecule, or instead of the reaction product, an equivalent amount of acrylic and/or methacrylic acid, which is then reacted during or after the polymerization reaction with the glycidyl ester of a monocarboxylic acid branched at the alpha position and carrying 5 to 18 C atoms per molecule,

m6) if desired, a substantially acid group-free, ethylenically unsaturated monomer copolymerizable with (m1), (m2), (m3), (m4), and (m5) and different from (m1), (m2),

(m4), and (m5), or a mixture of such monomers,

whereby (m1), (m2), (m3), (m4), (m5), and (m6) are selected in type and amount such that the polyacrylate resin (b11) has the desired OH number, acid number, and the desired molecular weight.

For the preparation of the fine-particle solid acrylate copolymers (b11), suitable as components (m1) can be any (meth)acrylic acid alkyl esters or cycloalkyl esters having up to 20 carbon atoms in the alkyl radical and copolymerizable with (m2), (m3), (m4), (m5), and (m6), particularly methyl, ethyl, propyl, n-butyl, sec-butyl, tert-butyl, hexyl, ethylhexyl, stearyl, and lauryl acrylate or methacrylate; cycloaliphatic (meth)acrylic acid esters, particularly cyclohexyl, isobornyl, dicyclopentadienyl, octahydro-4,7-methano-1H-indenemethanol, or tert-butylcyclohexyl (meth)acrylate; (meth)acrylic acid oxaalkyl esters or oxacycloalkyl esters, such as ethyl triglycol (meth)acrylate and methoxyoligo glycol (meth)acrylate with a molecular weight Mn of preferably 550; or other ethoxylated and/or propoxylated hydroxyl group-free (meth)acrylic acid derivatives. These may contain in minor amounts higher functional (meth)acrylic acid alkyl esters or cycloalkyl esters, such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butylene glycol, pentane-1,5-diol, hexane-1,6-diol, octahydro-4,7-methano-1H-indenedimethanol, or cyclohexane-1,2-, -1,3-, or -1,4-diol di(meth)acrylate; trimethylolpropane di- or tri(meth)acrylate; or pentaerythritol di-, -tri-, or tetra(meth)acrylate. Within the scope of the present invention, minor amounts of higher functional monomers are understood to be such amounts that do not lead to crosslinking or gelation of the polyacrylate resins.

Suitable as component (m2) are ethylenically unsaturated monomers, which are copolymerizable with (m1), (m2), (m3), (m4), (m5), and (m6) and different from (m5), carry at least one hydroxyl group per molecule, and are substantially free of acid groups, such as hydroxyalkyl esters of acrylic acid, methacrylic acid, or another alpha,beta-ethylenically unsaturated carboxylic acid, which derive from an alkylene glycol, esterified with the acid, or can be obtained by reacting the acid with an alkylene oxide, in particular hydroxyalkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid, or itaconic acid, in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl,

3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl acrylate or methacrylate, ethacrylate, crotonate, maleate, fumarate, or itaconate; 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, monomaleinate, monofumarate, or monoitaconate; or reaction products of cyclic esters, such as, e.g., epsilon-caprolactone and hydroxyalkyl esters thereof; or olefinically unsaturated alcohols, such as allyl alcohol, or polyols such as trimethylolpropane mono- or diallyl ether or pentaerythritol mono-, di-, or triallyl ethers. The statements made for he higher functional monomers (a1) also apply analogously to these higher functional monomers (m2). The proportion of trimethylolpropane monoallyl ether typically constitutes 2 to 10% by weight, based on the total weight of the monomers (m1) to (m6) employed for the preparation of the polyacrylate resin. In addition, it is also possible, however, to add 2 to 10% by weight of trimethylolpropane monoallyl ether to the prepared polyacrylate resin, based on the total weight of the monomers used for the preparation of the polyacrylate resin. The olefinically unsaturated polyols, such as in particular trimethylolpropane monoallyl ether, can be used as the sole hydroxyl group-containing monomers, in particular, however, proportionally in combination with other cited hydroxyl group-containing monomers.

Suitable as component (m3) is any ethylenically unsaturated monomer carrying at least one acid group, preferably one carboxyl group per molecule and copolymerizable with (m1), (m2), (m4), (m5), and (m6), or a mixture of such monomers. Acrylic acid and/or methacrylic acid are used especially preferably as component (m3). Other ethylenically unsaturated carboxylic acids having up to 6 C atoms in the molecule can also be used, however. Examples of such acids are ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid. Furthermore, ethylenically unsaturated sulfonic or phosphonic acids, or the partial esters thereof can be used as component (m3). In addition, maleic acid mono(meth)acryloyloxyethyl ester, succinic acid mono(meth)acryloyloxyethyl ester, and phthalic acid mono(meth)acryloyloxyethyl ester may be considered as component (m3).

One or more vinyl esters of monocarboxylic acids, branched in the alpha position and having 5 to 18 C atoms in the molecule, are used as component (m4). The branched monocarboxylic acid can

be obtained by reacting formic acid or carbon monoxide and water with olefins in the presence of a liquid, highly acidic catalyst; the olefins may be crack products of paraffinic hydrocarbons, such as mineral oil fractions, and may contain both branched and straight-chain acyclic and/or cycloaliphatic olefins. During the reaction of such olefins with formic acid or with carbon monoxide and water, a mixture of carboxylic acids forms, in which the carboxyl groups occur predominantly at a quaternary carbon atom. Other olefinic starting compounds are, e.g., propylene trimer, propylene tetramer, and diisobutylene. The vinyl esters, however, can also be prepared in a manner known per se from the acids, e.g., by reacting the acid with acetylene. Especially preferred, because of the good availability, are vinyl esters of saturated aliphatic monocarboxylic acids having 9 to 11 C atoms, which are branched at the alpha-C atom.

The reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of a monocarboxylic acid, branched at the alpha position and having 5 to 18 C atoms per molecule, is used as component (m5). Glycidyl esters of highly branched monocarboxylic acids can be obtained under the name "Cardura." The reaction of acrylic or methacrylic acid with the glycidyl ester of a carboxylic acid with a tertiary alpha-carbon atom may occur before, during, or after the polymerization reaction. The reaction product of acrylic and/or methacrylic acid with the glycidyl ester of Versatic acid is used preferably as component (m5). This glycidyl ester can be obtained commercially under the name "Cardura E10."

All substantially acid group-free, ethylenically unsaturated monomers, copolymerizable with (m1), (m2), (m3), (m4), and (m5) and different from (m1), (m2), (m3), and (m4), or mixtures of such monomers may be used as component (m6). Suitable as component (m6) are:

- Olefins, such as ethylene, propylene, but-1-ene, pent-1-ene, hex-1-ene, cyclohexene, cyclopentene, norbonene, butadiene, isoprene, cylopentadiene, and/or dicyclopentadiene;

- (Meth)acrylamides, such as (meth)acrylamide, and N-methyl, N,N-dimethyl, N-ethyl, N,N-diethyl, N-propyl, N,N-dipropyl, N-butyl, N,N-dibutyl, N-cyclohexyl, and/or N,N-cyclohexylmethyl (meth)acrylamide;

- Epoxy group-containing monomers, such as the glycidyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and/or itaconic acid;
- Vinyl aromatic hydrocarbons, such as styrene, alpha-alkyl styrenes, in particular alpha-methylstyrene, and/or vinyltoluene;
- Nitriles, such as acrylonitrile and/or methacrylonitrile;

Vinyl compounds, such as vinyl chloride, vinyl fluoride, vinylidene dichloride, vinylidene difluoride; N-vinylpyrrolidone; vinyl ethers such as ethylvinyl ether, n-propylvinyl ether, isopropylvinyl ether, n-butylvinyl ether, isobutylvinyl ether, and/or vinylcyclohexyl ether; vinyl esters, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, and/or the vinyl esters of 2-methyl-2-ethylheptanoic acid; and/or

- Polysiloxane macromonomers, which have a number average molecular weight Mn of 1000 to 40,000, preferably of 2000 to 20,000, especially preferably 2500 to 10,000, and in particular 3000 to 7000, and on average 0.5 to 2.5, preferably 0.5 to 1.5, ethylenically unsaturated double bonds per molecule, as they are described in DE-A 38 07 571 on pages 5 to 7, DE-A 37 06 095 in columns 3 to 7, EP-B 0 358 153 on pages 3 to 6, in USA 4,754,014 in columns 5 to 9, in DE-A 44 21 823, or in the international patent application WO 92/22615 on page 12, line 18, to page 18, line 10, or acryloxysilane-containing vinyl monomers, prepared by reaction of hydroxy-functional silanes with epichlorohydrin and subsequent reaction of the reaction product with methacrylic acid and/or hydroxyalkyl esters of (meth)acrylic acid.

Preferably, vinyl aromatic hydrocarbons (m6) are used.

The type and amount of the components (m1) to (m6) are selected such that the fine-particle solid acrylate copolymer (b11) has the desired OH number, acid number, and glass transition temperature.

From the process standpoint, the preparation of the acrylate copolymers (b11), to be used as taught by the invention, has no special features, but is carried out with use of conventional and prior-art processes of copolymerization in bulk, solution, or emulsion or by suspension or precipitation polymerization

Polymerization initiators are advantageously employed in the preparation of acrylate copolymers (b11), used preferentially according to the invention.

Examples of suitable polymerization initiators are free radical-forming initiators, such as, e.g., tert-butylperoxyethyl hexanoate, benzoyl peroxide, di-tert-amyl peroxide, azobisisobutyronitrile, and tert-butyl perbenzoate. The initiators are employed preferably in an amount from 1 to 25% by weight, especially preferably from 2 to 10% by weight, based on the total weight of the monomers.

The polymerization is carried out expediently at a temperature of 80 to 200°C, preferably 110 to 180°C. Ethoxyethyl propionate and isopropoxypropanol are preferably used as solvents.

The acrylate copolymer (b11) is preferably prepared by a two-step process, because in this way the resulting coating materials have a better processibility. For this reason, acrylate copolymers (b11) are used preferably, which are obtained

1. by polymerizing a mixture of (m1), (m2), (m4), (m5), and (m6) or a mixture of portions of components (m1), (m2), (m4), (m5), and (m6) in an organic solvent,

2. after at least 60% by weight of the mixture consisting of (m1), (m2), (m4), (m5), and if desired (m6) has been added, by adding (m3) and the optionally present remainder of the components (m1), (m2), (m4), (m5), and (m6) and further polymerizing them, and

3. after the polymerization ends, by neutralizing the obtained polyacrylate resin at least in part, i.e., by converting the acid groups into the corresponding acidic anion groups.

In addition, it is also possible, however, to charge initially components (m4) and/or (m5) together with at least one portion of the solvent and to meter in the remaining components. Furthermore, components (m4) and/or (m5) can also be added only partially together with at least one portion of the solvent into the initial charge, and the remainder of these components can be added, as described above. Preferably, for example, at least 20% by weight of the solvent and about 10% by weight of the component (m4) and (m5) and if desired portions of components (m1) and (m6) are charged initially.

Also preferred is the preparation of the acrylate copolymers (b11) by a two-step process, in

which the first step lasts 1 to 8 hours, preferably 1.5 to 4 hours, and the addition of the mixture of (m3) and the optionally present remainder of components (m1), (m2), (m4), (m5), and (m6) occurs within 20 to 120 min, preferably within 30 to 90 min. After the addition of the mixture of (a3) and the optionally present remainder of components (m1), (m2), (m4), (m5), and (m6) has ended, polymerization is continued until all employed monomers have been substantially totally reacted. In so doing, the second step can immediately follow the first step. However, the second step can be begun only after a certain amount of time has passed, for example, after 10 min to 10 hours.

The amount and addition rate of the initiator are selected such that a polyacrylate resin (b11) with the desired number average molecular weight Mn results. It is preferred that the initiator feed is begun some time, generally about 15 min, before the monomer feed. Furthermore, a process is preferred in which the initiator addition is begun at the same time as the monomer addition and ended about half an hour after the monomer addition has ended. The initiator is preferably added in a constant amount per unit time. After initiator addition has ended, the reaction mixture is kept at the polymerization temperature (as a rule for 1.5 hours) until all the employed monomers have been substantially totally reacted. "Substantially totally reacted" is intended to mean that preferably 100% by weight of the employed monomers has been reacted but it is also possible that a low residual monomer content of at most up to about 0.5% by weight, based on the weight of the reaction mixture, may remain unreacted.

Preferably, the monomers for the preparation of the acrylate copolymers (b11) are polymerized at a not too high polymerization solid, preferably a polymerization solid of 80 to 50% by weight, based on the comonomers, and then the solvent is removed in part by distillation, so that the forming acrylate copolymer solutions (b11) have a solids content of preferably 100 to 60% by weight.

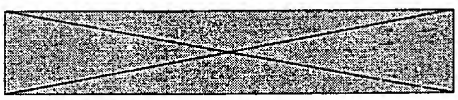
Methods, conventional and known in the plastics field, of continuous or discontinuous copolymerization under normal pressure or excess pressure in stirred tanks, autoclaves, tubular reactors, or Taylor reactors are used in the preparation of the fine-particle solid acrylate

copolymers (b11), to be used as taught by the invention.

Examples of suitable (co)polymerization processes for the preparation of the acrylate copolymer (A1) are described in the patents DE-A 197 09 465, DE-C 197 09 476, DE-A 28 48 906, DE-A 195 24 182, EP-A 0 554 783, WO 95/27742, DE-A 38 41 540, or WO 82/02387.

Taylor reactors are used advantageously, in particular for copolymerization in bulk, solution, or emulsion.

Taylor reactors, which are used in the conversion of materials under the conditions of Taylor flow, are prior in the art. They consist substantially of two coaxial, concentrically arranged cylinders, of which the outer cylinder is stationary and the inner cylinder rotates. The space formed by the gap between the cylinders serves as the reaction space. With increasing angular velocity ω_i of the inner cylinder, a series of different flow patterns form, which are characterized by a dimensionless characteristic, the so-called Taylor number Ta. The Taylor number, in addition to the angular velocity of the stirrer, is also still dependent on the kinematic viscosity ν of the fluid in the gap and on the geometric parameters, the outer radius of the inner cylinder r_i, the inner radius of the outer cylinder r_a, and the gap width d, the difference between the two radii, according to the following formula:



with $d = r_a - r_i$.

At a lower angular velocity, laminar Couette flow, a simple drag flow, forms. If the rotational velocity of the inner cylinder is increased further, above a critical value alternately oppositely rotating (contrarotating) vortexes with axes longitudinal to the circumferential direction occur. These so-called Taylor vortexes are rotationally symmetric and have a diameter that is approximately as large as the gap width. Two neighboring vortexes form a vortex pair or a vortex cell.

This behavior depends on the fact that during the rotation of the inner cylinder with a resting outer cylinder, the fluid particles in the vicinity of the inner cylinder are exposed to a greater centrifugal force than those farther removed from the inner cylinder. This difference in the acting centrifugal forces pushes the fluid particles from the inner to the outer cylinder. The viscosity force works against the centrifugal force, because friction must be overcome during the movement of fluid particles. If the rotational velocity increases, then the centrifugal force also

increases. Taylor vortexes arise, if the centrifugal force is greater than the stabilizing viscosity force.

In the case of Taylor flow with a low axial current, each vortex pair wanders through the gap, whereby only a minor exchange of materials between neighboring vortex pairs occurs. The mixing within such a vortex pair is very high, whereas the axial mixing outside the pair limits is only very low. A vortex pair can therefore be regarded as a well-mixed stirred tank. The flow system thus behaves as an ideal flow tube, in that the vortex pair wanders through the gap with a constant residence time like an ideal stirred tank.

Advantageous in this case as taught by the invention are Taylor reactors with an outer reactor wall and a present therein concentrically or eccentrically disposed rotor, a reactor bottom, and a reactor lid, which together define the annular gap-shaped reactor volume, at least one device for metering in the educts, and a device for product discharge, whereby the reactor wall and/or the rotor are (or is) geometrically designed such that the conditions for the Taylor flow are fulfilled along substantially the entire reactor length within the reactor volume; i.e., the annular gap expands in the flow-through direction.

Polyester resins (b12) in particular, which are obtained by reacting

p1) optionally sulfonated polycarboxylic acids or the esterifiable derivatives thereof, if desired, together with monocarboxylic acids,

p2) polyols, optionally together with monools,

p3) optionally other modifying components, and

p4) optionally a component reactive with the reaction product of (pl), (p2), and optionally (p3),

are used in the mixed coating compositions (B).

Examples of polycarboxylic acids, which may be used as component (p1), are aromatic, aliphatic, and cycloaliphatic polycarboxylic acids. Aromatic and/or aliphatic polycarboxylic acids are used preferentially as component (p1).

Examples of suitable polycarboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, phthalic acid monosulfonate, isophthalic acid monosulfonate, or terephthalic acid, halophthalic acids, such as tetrachloro- or tetrabromophthalic acid, adipic acid, glutaric acid, azelaic acid, sebacic acid, fumaric acid, maleic acid, trimellitic acid, pyromellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 4-methylhexahydrophthalic acid, endomethylenetetrahydrophthalic acid, tricyclodecanedicarboxylic acid, endoethylenehexahydrophthalic acid, camphoric acid, cyclohexanetetracarboxylic acid, or cyclobutanetetracarboxylic acid. The cycloaliphatic polycarboxylic acids can be used in both their cis and trans form, as well as a mixture of both forms. Also suitable are the esterifiable derivatives of the aforementioned polycarboxylic acids, such as, e.g., their mono- or polyvalent esters, with aliphatic alcohols having 1 to 4 C atoms or hydroxyalcohols having 1 to 4 C atoms. In addition, the anhydrides of the aforementioned acids can be used, provided they exist.

If desired, together with the polycarboxylic acids, monocarboxylic acids can also be used, such as, for example, benzoic acid, tert-butylbenzoic acid, lauric acid, isononanoic acid, and fatty acids of naturally occurring oils. Isononanoic acid is used preferably as the monocarboxylic acid.

Suitable alcohol components (p2) for the preparation of the polyester (A2) are polyhydric alcohols, such as ethylene glycol, propanediols, butanediols, hexanediols, hydroxypivalic acid neopentyl esters, neopentyl glycol, diethylene glycol, cyclohexanediol, cyclohexanedimethanol, trimethylpentanediol, ethylbutylpropanediol, ditrimethylolpropane, trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, trishydroxyethylisocyanate, polyethylene glycol, polypropylene glycol, if desired together with monohydric alcohols, such as, for example, butanol, octanol, lauryl alcohol, cyclohexanol, tert-butylcyclohexanol, and ethoxylated or propoxylated phenols.

Suitable as component (p3) for the preparation of the polyester (b12) are in particular compounds that have a group reactive with the functional groups of the polyesters, with the exception of the compounds recited as component (p4). Used preferably as the modifying component (p3) are

polyisocyanates and/or diepoxide compounds, if desired also monoisocyanates and/or monoepoxide compounds. Suitable components (p3) are described, for example, in DE-A 40 24 204 on page 4, lines 4 to 9.

Suitable as component (p4) for the preparation of the polyester resins (b12) are compounds that have, in addition to a group reactive with the functional groups of the polyester (b12), further a tertiary amino group, for example, monoisocyanates with at least one tertiary amino group, or mercapto compounds with at least one tertiary amino group. We refer to DE-A 40 24 204, page 4, lines 10 to 49, for details.

The preparation of the polyester resins (b12) occurs with the use of known methods for esterification, as they are described, for example, in DE-A 40 24 204, page 4, lines 50 to 65. The reaction occurs thereby typically at temperatures between 180 and 280°C, if desired, in the presence of a suitable esterification catalyst, such as, e.g., lithium octoate, dibutyltin oxide, dibutyltin dilaurate, or para-toluenesulfonic acid.

The preparation of the polyester resins (b12) is typically carried out in the presence of low amounts of a suitable solvent as an entraining agent. Aromatic hydrocarbons, such as in particular xylene and (cyclo)aliphatic hydrocarbons, e.g., cyclohexane or methylcyclohexane, are used as entraining agents.

Special preference is given to the use of polyester resins (b12), which have been prepared by a two-step process in which first a hydroxyl group-containing polyester with an OH number of 100 to 300 mg of KOH/g, an acid number of less than 10 mg of KOH/g, and a number average molecular weight of 500 to 2000 dalton is prepared, which is then reacted in a second step with carboxylic acid anhydrides to the desired polyester resin (b12). The amount of carboxylic acid anhydrides in so doing is selected such that the obtained polyester resin (b12) has the desired acid number. Suitable for this reaction are all typically used acid anhydrides, such as, e.g., hexahydrophthalic anhydride, trimellitic anhydride, pyromellitic anhydride, phthalic anhydride, camphoric anhydride, tetrahydrophthalic anhydride, succinic anhydride, and mixtures of these and/or other anhydrides and in particular anhydrides of aromatic polycarboxylic acids, such as

trimellitic anhydride.

It is possible if desired that the acrylate copolymer (b12) has been prepared at least partially in the presence of the polyester resin (b12). Advantageously, in this case, at least 20% by weight and especially advantageously 40 to 80% by weight of the acrylate copolymer (b11) is prepared in the presence of the polyester resin (b12). The optionally remaining amount of the acrylate copolymer (b11) is then added to the mixed coating composition (B). In so doing, it is possible that this already polymerized resin has the same monomer composition as the acrylate copolymer (b11) synthesized in the presence of polyester resin (b12). A hydroxyl group-containing acrylate copolymer (b11) with a different monomer composition can also be added, however. In addition, it is also possible to add a mixture of different acrylate copolymers (b11) and/or polyester resins (b12), whereby if desired a resin has the same monomer composition as the acrylate copolymer (b11) synthesized in the presence of the polyester resin (b12).

Suitable hydroxyl group and acid group-containing polyurethane resins (b13), to be used as taught by the invention, are described, for example, in the following publications: EP-A 0 355 433, DE-A 35 45 618, DE-A 38 13 866, DE-A 32 10 051, DE-A 26 24 442, DE-A 37 39 332, US-A 4,719,132, EP-A 0 089 497, US-A 4,558,090, US-A 4,489,135, DE-A 36 28 124, EP-A 0 158 099, DE-A 29 26 584, EP-A 0 195 931, DE-A 33 21 180, and DE-A 40 05 961.

Polyurethane resins (b13), which can be prepared by the reaction of isocyanate group-containing prepolymers with isocyanate-reactive compounds, are used in particular in the mixed coating composition (B).

The preparation of isocyanate group-containing prepolymers can occur by reacting polyols with a hydroxyl number of 10 to 1800, preferably 50 to 1200 mg of KOH/g, with excess polyisocyanates at temperatures of up to 150°C, preferably 50 to 130°C, in organic solvents, which cannot react with isocyanates. The equivalent ratio of NCO groups to OH groups is between 2.0 : 1.0 and > 1.0 : 1.0, preferably between 1.4 : 1 and 1.1 : 1.

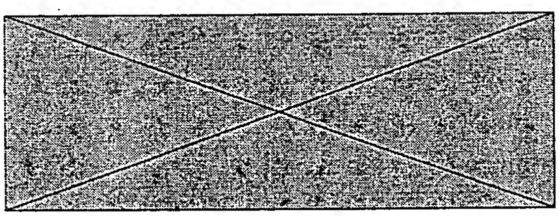
The polyols used for the preparation of the prepolymers may be low-molecular-weight and/or

high-molecular-weight and contain inactive anionic groups or groups capable of anion formation. Low-molecular-weight polyols with a molecular weight of 60 up to 400 dalton may also be used for the preparation of the isocyanate group-containing prepolymers. In so doing, amounts of up to 30% by weight of the entire polyol components, preferably about 2 to 20% by weight, are used.

To obtain an NCO prepolymer of high flexibility, a high proportion of a predominantly linear polyl with a preferred OH number from 30 to 150 mg of KOH/g should be added. Up to 97% by weight of the entire polyol can consist of saturated and unsaturated polyesters and/or polyethers with a number average molecular weight Mn of 400 to 5000 dalton. The selected polyether diols should not introduce an excess amount of ether groups, because otherwise the formed polymers swell in water. Polyester diols are prepared by esterification of organic dicarboxylic acids or their anhydrides with organic diols or derive from a hydroxycarboxylic acid or a lactone. To prepare branched polyester polyols, polyols or polycarboxylic acids with a higher valence can be used to a minor extent.

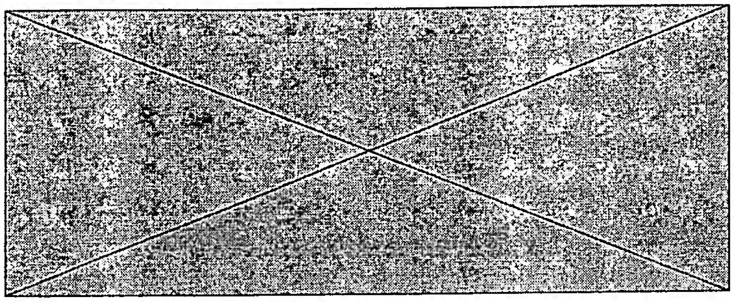
Preferably, the alcohol component used for the preparation of the polyurethane resins consists at least to a certain extent of

u_1) at least one diol of the formula (I')



in which R_1 and R_2 each represent the same or different radical and stand for an alkyl radical having 1 to 18 C atoms, an aryl radical, or a cycloaliphatic radical, with the proviso that R_1 and/or R_2 may not be methyl, and/or

u_2) at least one diol of the formula (II')



in which R_3, R_4, R_6, and R_7 each represent identical or different radicals, and stand for an alkyl radical having 1 to 6 C atoms, a cycloalkyl radical, or an aryl radical, and R_5 represents an alkyl radical having 1 to 6 C atoms, an aryl radical, or an unsaturated alkyl radical having 1 to 6 C atoms, and n is either 0 or 1.

All propanediols of formula (I'), in which either R_1 or R_2 or R_1 and R_2 are not methyl, are suitable as diols (u_1), such as, for example, 2-butyl-2-ethylpropanediol-1,3, 2-butyl-2-methylpropanediol-1,3, 2-phenyl-2-methylpropanediol-1,3, 2-propyl-2-ethylpropanediol-1,3, 2-di-tert-butylpropanediol-1,3, 2-butyl-2-propylpropanediol-1,3, 1-dihydroxymethylbicyclo[2.2.1]heptane, 2,2-diethylpropanediol-1,3, 2,2-dipropylpropanediol-1,3, 2-cyclohexyl-2-methylpropanediol-1,3, and others.

For example, 2,5-dimethylhexanediol-2,5, 2,5-diethylhexanediol-2,5, 2-ethyl-5-methylhexanediol-2,5, 2,4-dimethylpentanediol-2,4, 2,3-dimethylbutanediol-2,3, 1,4-(2'-hydroxypropyl)benzene, and 1,3-(2'-hydroxypropyl)benzene can be used as diols (u_2) (formula (II')).

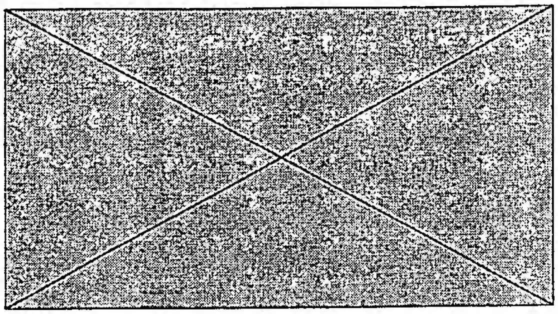
Preferred as diols (u_1) are 2-propyl-2-ethylpropanediol-1,3, 2,2-diethylpropanediol-1,3, 2-butyl-2-ethylpropanediol-1,3, and 2-phenyl-2-ethylpropanediol-1,3 and as component (u_2) 2,3-dimethylbutanediol-2,3 and 2,5-dimethylhexanediol-2,5. Especially preferred as component (a_1) [sic] are 2-butyl-2-ethylpropanediol-1,3 and 2-phenyl-2-ethylpropanediol-1,3 and as component (u_2) 2,5-dimethylhexanediol-2,5.

The diols (u_1) and/or (u_2) are typically used in an amount of 0.5 to 15% by weight, preferably 1 to 7% by weight, in each case based on the total weight of the constituent components used for the preparation of the polyurethane resin (A3).

Aliphatic, cycloaliphatic, and/or aromatic polyisocyanates having at least two isocyanate groups per molecule are used as typical multifunctional isocyanates for the preparation of the polyurethane resins (b13). Preferred are the isomers or isomer mixtures of organic diisocyanates. Because of their good resistance to UV light, (cyclo)aliphatic diisocyanates afford products with a low yellowing tendency. The polyisocyanate components used for the formation of the prepolymer may also contain a proportion of polyisocyanates with a higher valence, provided that no yellowing is caused by this. Products, which arise by trimerization or oligomerization of diisocyanates or by reaction of diisocyanates with polyfunctional OH or NH groups, have proven successful as triisocyanates. The average functionality can be reduced if desired by addition of monoisocyanates.

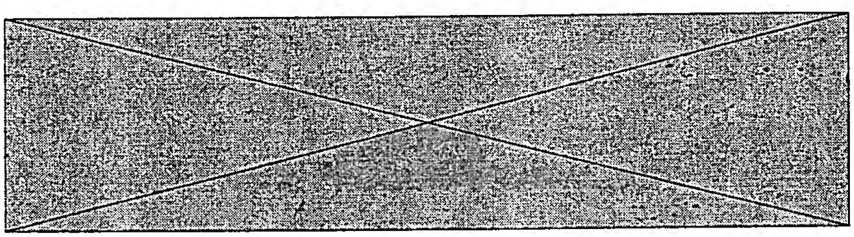
Phenylene diisocyanate, toluylene diisocyanate, xylylene diisocyanate, bisphenylene diisocyanate, naphtylene diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate, cyclobutane diisocyanate, cyclopentylene diisocyanate, cyclohexylene diisocyanate, methylcyclohexylene diisocyanate, dicyclohexylmethane diisocyanate, ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylethylene diisocyanate, and trimethylhexane diisocyanate can be cited as examples of usable polyisocyanates.

For the preparation of high-solids polyurethane solutions (b13), diisocyanates of the general formula (III')



are used in particular, whereby X stands for a bivalent, aromatic hydrocarbon radical, preferably for an optionally halogen-, methyl-, or methoxy-substituted naphthylene, diphenylene, or 1,2-, 1,3-, or 1,4-phenyl radical, especially preferably for a 1,3-phenylene radical, and R_1 and R_2 for an alkyl radical having 1 to 4 C atoms, preferably for a methyl radical. Diisocyanates of the formula (III') are known (their preparation is described, for example, in EP-A 101 832, US-A 3,290,350, US-A 4,130,577, and US-A 4,439,616) and can be obtained in some cases commercially (1,3-bis-(2-isocyanatoprop-2-yl)benzene, is sold, for example, by American Cyanamid Company under the trade name TMXDI (META)®).

Preferred further as polyisocyanate components are diisocyanates of the formula (IV')



where: R stands for a bivalent alkyl or aralkyl radical having 3 to 20 carbon atoms and R' for a bivalent alkyl or aralkyl radical having 1 to 20 carbon atoms;

in particular, 1-isocyanato-2-(3-isocyanatoprop-1-yl)cyclohexane.

Polyurethanes are generally not compatible with water, if special components are not

incorporated during their synthesis and/or special preparation steps are not taken. Thus, in the preparation of the polyurethane resins (b13), compounds can be used, which contain two isocyanate-reactive H-active groups and at least one group that assures dispersibility in water. Suitable groups of this type are the aforementioned nonionic groups (iii) (e.g., polyether), the aforementioned anionic groups (ii), mixtures of these two groups, or the aforementioned cationic groups (i).

Thus, such a high acid number can be built into the polyurethane resin (b13) that the neutralized product can be stably dispersed in water. Compounds are used for this purpose, which contain at least one isocyanate-reactive group and at least one group (ii) capable of anion formation. Suitable isocyanate-reactive groups are in particular hydroxyl groups and primary and/or secondary amino groups. Groups (ii), which are capable of anion formation, are carboxyl groups, sulfonic acid groups, and/or phosphonic acid groups. Preferably, alkanoic acids with two substituents at the alpha-carbon atom are used. The substituent can be a hydroxyl group, an alkyl group, or an alkylol group. These polyols have at least 1, generally 1 to 3 carboxyl groups in the molecule. They have 2 to about 25, preferably 3 to 10 carbon atoms. The carboxyl group (ii)-containing polyol can constitute 3 to 100% by weight, preferably 5 to 50% by weight, of the total polyol constituent in the NCO prepolymer.

The amount, available in salt form by means of carboxyl group neutralization, of ionizable carboxyl groups (ii) generally constitutes at least 0.4% by weight, preferably at least 0.7% by weight, based on the solid. The upper limit is about 12% by weight. The amount of dihydroxyalkanoic acids in the nonneutralized prepolymer affords an acid number of at least 5 mg of KOH/g, preferably at least 10 mg of KOH/g. With very low acid numbers, further measures are generally necessary to achieve dispersibility in water. The top limit for the acid number is 150 mg of KOH/g, preferably 40 mg if KOH/g, based on the solid. Preferably, the acid number is in the range of 20 to 40 mg of KOH/g.

The isocyanate groups of the isocyanate group-containing prepolymer are reacted with a modifying agent or chain extension agent. In so doing, the modifying agent is preferably added

in such an amount that it results in chain extension and thereby in increases in molecular weight. Preferably organic compounds, which contain hydroxyl and/or secondary and/or primary amino groups, in particular di-, tri-, and/or higher functional polyamines and/or polyols, are used as the modifying agent. Examples of usable polyamines are ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, or diethylenetriamine. Examples of usable polyols are trimethylolpropane, 1,3,4-butanetriol, glycerol, erythritol, mesoerythritol, arabitol, adonitol, etc. Trimethylolpropane is used with preference.

For the preparation of the polyurethane resin (b13), preferably a prepolymer with isocyanate groups is prepared first, from which then by further reaction, preferably by chain extension, the desired polyurethane resin (b13) is prepared. In so doing, the components are reacted using well-known processes of organic chemistry (cf., e.g., *Kunststoff-Handbuch* [Plastics Handbook], Vol. 7: *Polyurethane* [Polyurethanes], edited by Dr. Y. Oertel, Carl Hanser Verlag, Munich, Vienna, 1983). Examples for the preparation of the prepolymers are described in DE-A 26 24 442 and DE-A-32 10 051. The preparation of the polyurethane resins (b13) can proceed with use of known processes (e.g., acetone processes).

The components are reacted preferably in ethoxyethyl propionate (EEP) as the solvent. The amount of EEP can be varied over broad ranges thereby and should be sufficient for the formation of a prepolymer solution with an appropriate viscosity. In general, up to 70% by weight, preferably 5 to 50% by weight, and especially preferably less than 20% by weight of solvent, based on the solids, is used. Thus, the reaction can be carried out, for example, very especially preferably with a solvent content of 10–15% by weight of EEP, based on the solids.

The reaction of components can occur if desired in the presence of a catalyst, such as organotin compounds and/or tertiary amines.

For the preparation of the prepolymers, the amounts of the components are selected such that the equivalent ratio of NCO to OH groups is between 2.0 : 1.0 and > 1.0 : 1.0, preferably between 1.4 : 1 and 1.1 : 1.

The NCO prepolymer contains at least about 0.5% by weight of isocyanate groups, preferably at least 1% by weight of NCO, based on the solids. The upper limit is about 15% by weight, preferably 10% by weight, especially preferably 5% by weight of NCO.

The water-soluble or -dispersible fine-particle solid binders (b1), to be used as taught by the invention, can be present individually or as a mixture.

If they are to be used as a mixture, care should be taken that no fine-particle solid binders (b1), which contain functional groups (i), are combined with fine-particle solid binders (b1), which contain functional groups (ii), because this may lead to the formation of insoluble polyelectrolyte complexes.

Moreover, the fine-particle solid binders (b1) can contain further the binders (a1) described below, which are not soluble or dispersible in water as such, but which in the presence of the water-soluble or dispersible binders (b1) can be dispersed in water. Examples of suitable, water-insoluble or not water-dispersible binders (a1) stem from the aforementioned oligomer and/or polymer classes, but they contain no or only a few hydrophilic functional groups (i), (ii), or (iii), so that no water solubility or dispersibility results.

If during the preparation of the coating materials of the invention, the mixing of the components, particularly of modules (I), (II), and (III), is to occur by means of manual stirring, it is advantageous for the coating material of the invention, if the fine-particle solid binders (b1) are selected such that their 50% solution in ethoxyethyl propionate at 23°C has a viscosity of $\leq$ 10 dPas. If mixing by machine is to occur, higher-viscosity binders (b1) can be used, the 50%

solution of which in ethoxyethyl propionate at 23°C has a viscosity of ≤ 100 dPas. The top limit of the viscosity is created only by the performance of the mixer.

The particle size of the fine-particle solid binders (b1) is not critical. It is essential that the particle size is not set so small that the particles tend to agglomerate and/or become respirable, or so large that the resolution or redispersion is impeded or prevented. As taught by the invention, particle sizes of 5 to 500 μm are advantageous.

The preparation of the fine-particle solid binders (b1) has no special procedural features, but occurs, as described above, by conventional and known methods of polymerization in bulk, solution, or emulsion, or by suspension or precipitation polymerization and drying of the resulting binders (b1) with use of conventional and known methods and devices and under conditions that assure the formation of fine-particle solid products. Examples of suitable drying methods are spray drying, freeze drying, and precipitation from solution, emulsion, or suspension.

The fine-particle solid binders (b1) can also be present, however, in the form of a powder slurry, which is dried by the cited drying methods. In this case, the optionally present components, described below, may be present in the powder slurry particles. Powder slurries and their preparation are conventional and known and are described, for example, in the patents EP-A 0 652 264, US-A 4,268,542, DE-A 196, 13 547, or DE-A 195 18 392.

In many cases, it is advantageous to convert the binders (b1) after their preparation by addition of aqueous media (C), which contain at least one of the aforementioned neutralizing agents, into a secondary dispersion, which is then dried. It is also possible, however, to neutralize the binders (b1) before the addition of the aqueous media (C) with at least one of the aforementioned neutralizing agents and then to convert into a secondary dispersion.

During polymerization in solution, solvents are used which do not impede drying, but can be easily removed from the binders (b1). Preferably, solvents with a comparatively high vapor pressure are used. This also applies to cosolvents, which if desired are used in emulsion suspension, or precipitation polymerization, or for the preparation of the secondary dispersions, or to the nonsolvents, which are used for precipitation.

In addition to the binders (b1), the mixed coating composition (B) may contain as component (b2) pigments and/or fillers typical for coating compositions. In so doing, both pigments and fillers, which are typical for aqueous coating agents and do not react with water or do not dissolve in water, and also the pigments and fillers typically used in conventional coating agents may be used. The pigments and fillers can consist of inorganic or organic compounds and can be effect- and/or color-imparting. The coating material of the invention therefore, based on this multitude of suitable pigments and fillers, assures a universal range of uses for the coating materials and enables the realization of a multitude of color tones and optical effects.

Metal flake pigments, such as commercially available aluminum bronzes, aluminum bronzes chromatized in accordance with DE-A 36 36 183, and commercial stainless-steel bronzes, and nonmetallic effect pigments, such as, for example, pearlescent or interference pigments may be used as effect pigments (b2). Examples of suitable inorganic color-imparting pigments are titanium dioxide, iron oxides, sicotrans yellow, and carbon black. Examples of suitable organic color-imparting pigments are indanthrene blue, cromophthal red, irgazine orange, and heliogen green. Examples of suitable fillers are chalk, calcium sulfates, barium sulfate, silicates such as talk or kaolin, silicic acids, oxides such as aluminum hydroxide or magnesium hydroxide, nanoparticles, or organic fillers such as textile fibers, cellulose fibers, polyethylene fibers, or wood flour.

The coating agent of the invention can furthermore contain crosslinking agents (b3); it is essential that the crosslinking agent (b3) does not adversely affect the storage stability of the mixed coating composition (B), perhaps by premature crosslinking. One skilled in the art, for this reason, can select in a simple manner the suitable combinations of crosslinking agents (b3), on the one hand, and binders (b1), on the other.

Examples of suitable crosslinking agents (b3) are blocked di- and/or polyisocyanates.

Examples of suitable di- and/or polyisocyanates are organic polyisocyanates, in particular, so-called surface-coating polyisocyanates, having aliphatic, cycloaliphatic, araliphatic, and/or aromatically bound free isocyanate groups. Preference is given to the use of polyisocyanates

having 2 to 5 isocyanate groups per molecule and viscosities of 100 to 10,000, preferably 100 to 5000, and—if manual mixing of components (I), (II), and (III) is planned—in particular 1000 to 2000 mPas (at 23°C). If desired, small quantities of an organic solvent, preferably 1 to 25% by weight based on pure polyisocyanate, can also be added to the polyisocyanates in order thus to improve the ease of incorporation of the isocyanate and, if appropriate, to reduce the viscosity of the polyisocyanate to a value within the abovementioned ranges. Examples of solvents suitable as additives for the polyisocyanates are ethoxyethyl propionate, amyl methyl ketone, or butyl acetate.

In addition, the polyisocyanates can be modified hydrophilically or hydrophobically in a conventional and known manner.

Examples of suitable polyisocyanates are described, for example, in "*Methoden der organischen Chemie*" [Methods of Organic Chemistry], Houben-Weyl, Volume 14/2, 4th edition, Georg Thieme Verlag, Stuttgart 1963, page 61 to 70, and by W. Siefken, *Liebigs Ann. Chem.* Vol. 562, 75 to 136. Examples of those suitable are the isocyanates mentioned in the description of the polyurethane resins (b13) and/or isocyanate group-containing polyurethane prepolymers, which can be prepared by reaction of polyols with excess polyisocyanates and preferably have a low viscosity.

Further examples of suitable polyisocyanates are polyisocyanates having isocyanurate, biuret, allophanate, iminooxadiazinedione, urethane, urea, and/or uretdione groups. Polyisocyanates containing urethane groups, for example, are obtained by reacting some of the isocyanate groups with polyols, such as, e.g., trimethylolpropane and glycerol. It is preferred to employ aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane-2,4'-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, or 1,3-bis(isocyanatomethyl)cyclohexane, diisocyanates, derived from dimeric fatty acids, as they are sold under the tradename DDI 1410 by the Henkel company, 1,8-diisocyanato-4-isocyanatomethyl octane, 1,7-diisocyanate-4-isocyanatomethylheptane, or 1-isocyanate-2-(3-

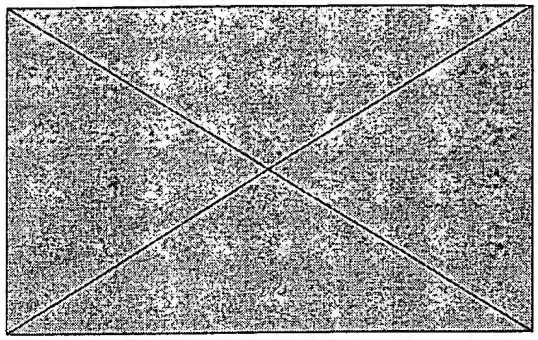
isocyanatopropyl)cyclohexane, or mixtures of these polyisocyanates.

Very particular preference is given to the use of mixtures of polyisocyanates which are based on hexamethylene diisocyanate and contain uretdione and/or isocyanurate groups and/or allophanate groups, as are formed by catalytic oligomerization of hexamethylene diisocyanate using appropriate catalysts. In addition, the polyisocyanate component may consist of any desired mixtures of the polyisocyanates mentioned by way of example.

Examples of suitable blocking agents are aliphatic, cycloaliphatic, or araliphatic monoalcohols, such as methyl, butyl, octyl, or lauryl alcohol, cyclohexanol, or phenylcarbinol; hydroxylamines such as ethanolamine; oximes such as methylethyl ketone oxime, acetone oxime, or cyclohexanone oxime; amines such as dibutylamine or diisopropylamine; CH-acid compounds such as malonic acid diester or acetoacetic acid ethyl ester; heterocycles such as dimethylpyrazole; and/or lactams such as epsilon-caprolactam.

Further examples of suitable crosslinking agents (b3) are polyepoxides (b3), in particular all known aliphatic and/or cycloaliphatic and/or aromatic polyepoxides, for example, based on bisphenol A or bisphenol F. Suitable as polyepoxides (b3) are, for example, also the polyepoxides commercially obtainable under the designations Epikote® from Shell, Denacol® from Nagase Chemicals Ltd., Japan, for example, Denacol EX-411 (pentaerythritol polyglycidyl ether), Denacol EX-321 (trimethylolpropane polyglycidyl ether), Denacol EX-512 (polyglycerol polyglycidyl ether), and Denacol EX-521 (polyglycerol polyglycidyl ether).

Tris(alkoxycarbonylamino)triazines of the formula



can also be used as crosslinking agents (b3).

Examples of suitable tris(alkoxycarbonylamino)triazines (b3) are described in the patents US-A 4,939,213, US-A 5,084,541, or EP-A 0 624 577. Tris(methoxy-, tris(butoxy-, and/or tris(2-ethylhexoxycarbonylamino)triazines are used particularly.

Methyl-butyl mixed esters, butyl-2-ethylhexyl mixed esters, and butyl esters are advantageous. Compared with the pure methyl ester, these have the advantage of better solubility in polymer melts and have a lower tendency for crystallization.

Aminoplasts, for example, melamine resins, can be used in particular as crosslinking agents (b3). In this case, any aminoplast, suitable for transparent topcoats or clearcoats, or a mixture of such aminoplasts can be used. In particular, the conventional and known aminoplasts may be suitable, the methylol groups and/or methoxymethyl groups of which are defunctionalized in part by means of carbamate or allophanate groups. Crosslinking agents of this type are described in the patents US-A 4 710 542 and EP-B 0 245 700 and in the article by B. Singh et al: "Carbamylmethylated Melamines, Novel Crosslinkers for the Coatings Industry" in *Advanced Organic Coatings Science and Technology Series*, 1991, Vol. 13, pages 193 to 207. Moreover, the aminoplasts may also be used binders (a1) in the base paint (A).

Further examples of suitable crosslinking agents (b3) are beta-hydroxyalkylamides, such as N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide or N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide.

Further examples of suitable crosslinking agents (b3) are siloxanes, in particular siloxanes with at least one trialkoxysilane or dialkoxysilane group.

Furthermore, the mixed coating composition (B) may contain auxiliaries and/or additives (b4), such as UV absorbers, radical traps; catalysts for crosslinking, in particular, organometallic compounds, preferably tin and/or organobismuth compounds, or tertiary amines; slip additives; polymerization inhibitors; defoamers; coupling agents; flow improvers, or film-forming auxiliaries, e.g., cellulose derivatives; or other additives typically present in coating materials

In particular, at least one rheology-controlling additive may be used as the auxiliary and additive (b4). Examples of suitable rheology-controlling additives (b4) are those known from patents WO 94/22968, EP-A 0 276 501, EP-A 0 249 201, or WO 97/12945; crosslinked polymeric microparticles, as have been disclosed, for example, in EP-A 0 008 127; inorganic layered silicates, such as aluminum-magnesium silicates, sodium-magnesium and sodium-magnesium-

fluorine-lithium layered silicates of the montmorillonite type; silicic acids such as aerosils; or synthetic polymers with ionic and/or associatively acting groups, such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride or ethylene-maleic anhydride copolymers and derivatives thereof, or hydrophobically modified ethoxylated urethanes or polyacrylates. Polyurethanes and/or layered silicates are employed preferably as rheology-controlling additives (b4).

Further, the mixed coating composition (B) may contain components (b5), which can be cured with actinic radiation, in particular UV radiation, and/or electron radiation. This offers the advantage that the coating materials of the invention can be cured both thermally and by radiation.

Basically all low-molecular-weight, oligomeric, and polymeric compounds, which can be cured by actinic radiation, in particular UV radiation, and/or electron radiation, as they are used conventionally in the field of UV-curable coating agents or coating agents curable with electron radiation, may be used as components (b5). These radiation-curable coating agents typically contain at least one, preferably several, radiation-curable binders, in particular based on ethylenically unsaturated prepolymers, and/or ethylenically unsaturated oligomers, if desired, one or more reactive diluents, and if appropriate one or more photoinitiators.

Advantageously, the radiation-curable binders are used as components (b5). Examples of suitable radiation-curable binders (b5) are (meth)acryl-functional (meth)acrylic copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates, and the corresponding methacrylates. Binders (b5) that are free of aromatic structural units are used preferably. For this reason, urethane (meth)acrylates and/or polyester (meth)acrylates are used preferably, and aliphatic urethane acrylates especially preferably.

The further essential component of the coating material of the invention is at least one base paint (A).

The base paint (A), to be used as taught by the invention, is again the essential component of the color and/or effect module to be used as taught by the invention.

The base paint (A), to be used as taught by the invention, contains at least one optionally water-soluble or -dispersible binder (a1). If a binder (a1) is used that is not water-soluble or -dispersible as such, it must be dispersible at least in the presence of the aforementioned water-soluble or -dispersible binders (b1). Examples of suitable binders (a1) not soluble or dispersible in water stem from the oligomer and/or polymer classes described above for binders (b1), but only if they contain no or only a few hydrophilic functional groups (i), (ii), or (iii), so that no water solubility or dispersibility results.

According to the invention, however, water-soluble or -dispersible binders (a1) are advantageous and are used preferentially for that reason. Examples of suitable water-soluble or dispersible binders (a1) are the binders (b1) described above. In this case, the base paint (A) may contain the binders (a1), which are different from the binders (b1). It is essential hereby to select binders (b1) and (a1) such that in the corresponding coating material of the invention no demixing results owing to polymer incompatibility. These can also be the same binders (a1 = b1). The variant to be preferred in the individual case is determined by the desired property profile of the coating material of the invention.

According to the invention, binders (a1) that have been prepared in the reactive diluents described below are advantageous.

Furthermore, the base paint (A), to be used as taught by the invention, contains at least one color- and/or effect-imparting pigment (a2).

Examples of suitable pigments (a2) are the aforementioned pigments (b2). In this case, the base paint (A) may also contain pigments (a2), which are different from the pigments (b2). For example, the color-imparting pigments (b2) can be present in the mixed coating composition (B) and the effect-imparting pigments (a2) in the base paint (A). These can also be the same pigments (a2 = b2).

In addition, the base paint (A), to be used as taught by the invention, contains at least one water-miscible organic solvent (a3).

Examples of suitable, water-miscible organic solvents (a3) are esters, ketones such as acetone methyl isobutyl ketone, keto esters, glycol ethers such as ethylene, propylene, or butylene glycol ether, glycol esters such as ethylene, propylene, or butylene glycol ester, or glycol ether esters such as ethoxyethyl propionate, or amides such as N-methylpyrrolidone or N,N-dimethylacetamide.

Further examples of suitable water-miscible organic solvents (a3) are so-called reactive diluents, which may participate in the reaction with the crosslinking agents (a5) and/or (b2).

Examples of suitable thermally crosslinkable reactive diluents (a3) are branched, cyclic, and/or acyclic C_9–C_{16} alkanes, which are functionalized with at least two hydroxyl groups, preferably dialkyl octanediols, in particularly the positional isomers of diethyl octanediols.
Other examples of suitable thermally crosslinkable reactive diluents (a3) are oligomeric polyols, which can be obtained by hydroformulation and subsequent hydrogenation from oligomeric intermediate products, which are recovered by metathetical reactions of acyclic monoolefins and cyclic monolefins; examples of suitable cyclic monoolefins are cyclobutene, cyclopentene, cyclohexene, cyclooctene, cycloheptene, norbonene, or 7-oxanorbonene; examples of suitable acyclic monoolefins are those present in hydrocarbon mixtures, which are obtained by cracking in petroleum refining (C_5 cut); examples of suitable oligomeric polyols to be used as taught by the invention have a hydroxyl number (OH number) of 200 to 450, a number average molecular weight Mn from 400 to 1000, and a weight average molecular weight Mw of 600 to 1100.

Further examples of suitable thermally crosslinkable reactive diluents (a3) are hyperbranched compounds with a tetrafunctional central group, derived from ditrimethylolpropane, diglycerol, ditrimethylolethane, pentaerythritol, tetrakis(2-hydroxyethyl)methane, tetrakis(3-hydroxypropyl)methane, or 2,2-bishydroxymethylbutanediol-(1,4) (homopentaerythritol). The preparation of these reactive diluents can proceed with use of conventional and known methods

for the preparation of hyperbranched and dendrimeric compounds. Suitable synthesis methods are described, for example, in the patents WO 93/17060 or WO 96/12754 or in the book by G.R. Newkome, C.N. Moorefield, and F. Vögtle, *Dendritic Molecules, Concepts, Syntheses, Perspectives*, VCH, Weinheim, New York, 1996.

Further examples of suitable reactive diluents (a3) are polycarbonate diols, polyester polyols, poly(meth)acrylate diols, or hydroxyl group-containing polyaddition products.

Examples of suitable reactive solvents (a3) are butyl glycol, 2-methoxypropanol, n-butanol, methoxybutanol, n-propanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, trimethylolpropane, 2-hydroxypropionic acid ethyl ester, or 3-methyl-3-methoxybutanol, as well as derivatives based on propylene glycol, e.g., ethoxyethyl propionate, isopropoxypropanol, or methoxypropyl acetate.

The base paint (A), to be used as taught by the invention, can furthermore contain at least one crosslinking agent (a5). Examples of suitable crosslinking agents (a5) are the aforementioned crosslinking agents (b2). In this case, the base paint (A) may contain crosslinking agents (a5), which differ from those present in the mixed coating composition (B). Moreover, the same crosslinking agents may be present (a5 = b2).

Not least, the base paint (A) can contain at least one auxiliary and/or additive (a6). Examples of suitable auxiliaries and additives are the aforementioned auxiliaries and additives (b4). Here as well, the base paint (A) may contain the same auxiliaries and/or additives as are present in the mixed coating composition (B) (a6 = b4). Because of the different functions of the base paint (A) and the mixed coating composition (B), however, generally different auxiliaries and additives (a6) and (b4) are used.

Furthermore, the base paint (A) can contain components (a7), which are curable with actinic radiation, in particular UV radiation, and/or electron radiation. This offers the advantage that the

coating materials of the invention are both thermally curable and radiation-curable. Examples of suitable components (a7) of this type are the aforementioned components (b5). In this case, the base paint (A) may contain the same components as are present in the mixed coating composition (B) (a7 = b5). Different components (a7) and (b5) may also be used, however.

The further major component of the coating material of the invention is the aqueous medium (C) or the dispersion module (III), the major component of which in turn is the aqueous medium (C). The aqueous medium (C) contains substantially water. In this case, the aqueous medium (C) may contain in minor amounts the binders (a1) or (b1), organic solvents (a3), neutralizing agents, crosslinking agents (a5) or (b3), and/or auxiliaries and/or additives (a6) or (b3), and/or other dissolved solid, liquid, or gaseous organic and/or inorganic, low- and/or high-molecular-weight substances, as were detailed above. Within the scope of the present invention, the term "minor amount" is understood to be an amount that does not offset the aqueous nature of the aqueous medium (C).

The aqueous medium (C) can also be pure water, however.

The composition of the coating materials of the invention can vary over a very broad range and is determined by its intended purpose. In this case, the quantitative ratios cited in the state of the art, in particular in the patents EP-A 0 578 645 or EP-A 0 608 773, can serve as a guideline. One skilled in the art therefore can determine for each application in a simple manner the most suitable composition from the state of the art or based on his general know-how, if appropriate with the aid of preliminary tests.

The preparation of the coating material of the invention can occur in any manner desired by combination of the aforementioned components in any sequence. As taught by the invention, however, it is advantageous to use the process of the invention.

The process of the invention is based on the preparation of at least one base paint (A) or at least one color- and/or effect-imparting module (1) by mixing the components (al) to (a3) as detailed above, and if appropriate (a4) to (a7).

Furthermore, at least one fine-particle solid mixed coating composition (B) or at least one solids module (II) is provided by mixing and drying of components (b1) and if appropriate (b2) to (b4).

Not least, at least one aqueous medium (C) or at least one dispersion module (III) is prepared.

The major components (A), (B), and (C) or the modules (I), (II), and (III) are combined together in another process step, whereby the coating material of the invention results. The sequence in which the major components or the modules can be mixed together can vary from coating material to coating material and can be determined by one skilled in the art in a simple manner from the state of the art and based on his general know-how, if appropriate with the aid of preliminary tests.

For example, the base paint (A) or the module (I) can be dispersed in the aqueous medium (C) or in the module (III), whereby the addition can occur all at once or in batches. Next, the mixed coating composition (B) or the module (II) can be added all at once or in batches to the mixture (A/C).

However, the mixed coating composition (B) or the module (II) can also be metered all at once or in batches into the aqueous medium (C) or the module (III) and be dissolved or dispersed herein. Next, the base paint (A) or the module (I) can be added all at once or in batches to the mixture (B/C).

Furthermore, the base paint (A) or the module (I) and the mixed coating composition (B) or the module (II) can be metered all at once or in batches into the aqueous medium (C) or the module (III) and be dissolved or dispersed herein.

Not least, the aqueous medium (C) or the module (III) can be metered all at once or in batches into the base paint (A) or the module (I), after which the mixed coating composition (B) or the module (II) is added. However, the mixed coating composition (B) or the module (II) during the addition of the aqueous medium (C) or the module (III) may already be present in the base paint (A) or the module (I).

It is essential for selecting a variant of the process of the invention that no phase separation and/or no precipitation of components occur during mixing.

After its preparation, the coating material of the invention can be adjusted to the viscosity, necessary for the application of the coating material, by adding additional aqueous medium (C).

The coating materials of the invention may be applied by conventional application methods, such as, e.g., spraying, knife coating, brushing, pouring, dipping, or rolling, to any substrate, such as, e.g., metal, wood, plastic, glass, or paper.

During their use in automotive refinishing, the coating materials of the invention are cured typically at temperatures below 120°C, preferably at temperatures of a maximum of 80°C. During their use in automotive production-line finishing, higher curing temperatures are also used.

The coating materials of the invention are used preferably for the preparation of topcoats. The coating materials of the invention can be used in both production-line finishing and refinishing of automobile bodies. They are used preferably in the field of refinishing and the coating of plastic parts.

The aqueous coating materials of the invention can be used as fillers and for the preparation of one-layer topcoats and as pigmented basecoats in a process for the preparation of multilayer coats (basecoat–clearcoat method).

Examples

Preparation Example 1

Preparation of an Aluminum-Containing Base Paint (A)

27 parts by weight of aluminum bronze, chromated according to patent DE-A 36 36 183, (Al content of 65% by weight, average particle diameter 15 μm) are homogeneously distributed in 27 parts by weight of butyl glycol by 15 min of stirring. Next, a mixture consisting of 10 parts by weight of butyl glycol and 36 parts by weight of a commercial, methyl-etherified melamine resin (75% by weight in isobutanol) is allowed to flow in with stirring. This mixture is stirred for another 30 min with a high-speed mixer at 1000 rpm.

Preparation Example 2

Preparation of a Polyurethane Dispersion for the Mixed Coating Composition (B)

2.1. Preparation of the Polyester Resin Solution

In a steel reactor suitable for polycondensation reactions, 4634 kg of Pripol® 1013 (dimeric fatty acid from Unichema), 1522 kg of 1,6-hexanediol, 1874 kg of isophthalic acid, and 331 kg of xylene as the entraining agent were weighed and heated to 150°C. The temperature of the mixture was raised to a maximum of 220°C such that the column head temperature of 125°C was not exceeded. Starting at an acid number of 5, the volatile components were distilled off, and the reaction was continued until an acid number of 3.5 was reached.

2. 2. Preparation of the Polyurethane Resin Dispersion

143.4 kg of the polyester resin solution according to Section 2.1 of this preparation example was heated together with 9.4 kg of dimethylolpropionic acid, 1.9 kg of neopentyl glycol, 50.5 kg of Desmodur® W (commercial polyisocyanate from Bayer), and 44 kg of methyl ethyl ketone to a constant isocyanate content. Next, 4.9 kg of trimethylolpropane was added based on a content of 1.1% by weight of isocyanate groups. When a viscosity range of 12 to 14 dPas was reached (measured 50% by weight in N-methylpyrrolidone), a further reaction was suppressed by addition of 2.7 kg of n-butanol. After 60 min of stirring at 82°C, 5.0 kg of dimethylethanolamine was added. After 30 min of stirring at 82°C, 34.2 kg of Pluriol P900 (commercial crosslinker from BASF AG) was added, after which the resulting mixture was stirred for another 30 min at 82°C.

Next, a solids content of 70% by weight (an hour at 130°C) was adjusted with methyl ethyl ketone, and 434.9 kg of deionized water was added. The solids content was 27.8% by weight, and the pH 7.82. The reaction mixture was homogeneous and free of specks and threads.

At a product temperature of 50 to 82°C, methyl ethyl ketone was removed by vacuum distillation except for a residual content of <0.5% by weight. After this, a solids content of 30.3% by weight was adjusted with deionized water. The pH of the resulting dispersion was 7.73.

The dispersion was in fact storage-stable for more than 4 weeks at 40°C with careful proper handling or under test conditions, but attack by microorganisms occurred frequently under operating conditions and/or during transport, because of which the dispersion became unusable.

Preparation Example 3

Preparation of a Mixed Coating Composition (B)

43 parts by weight of a preswollen aqueous paste, containing 3% by weight of an inorganic sodium–magnesium layered silicate thickening agent and 3% by weight of propylene glycol with a number average molecular weight of 900, whereby the percentages are based on the total weight of the paste, 19.8 parts by weight of deionized water, 0.5 parts by weight of a commercial defoamer, and 3.5 parts by weight of a 3.5% by weight solution of a commercial polyurethane thickener in water were added to 33.2 parts by weight of the polyurethane dispersion according to Preparation Example 2 with stirring.

The resulting mixture was converted by means of a spinning-disk atomizer dryer into the fine-particle, powdered mixed coating composition (B). The glass transition temperature of the mixed coating composition (B) was -38°C.

The mixed coating composition (B) was storage-stable virtually with no limit and showed no attack by microorganisms. Even after months of storage, it could be used without limitation for the preparation of the coating materials of the invention.

Example

Preparation of the Coating Material of the Invention

.... parts by weight of the mixed coating composition (B) according to Preparation Example 3 were dispersed or dissolved in .... parts by weight of deionized water in batches with stirring. .... parts by weight of the base paint (A) according to Preparation Example 1 were added with stirring to the resulting mixed coating composition solution (B/C). After homogenization, a coating material of the invention resulted, which was storage-stable. In its application properties, it was totally equal to the coating materials that were prepared as such in a conventional and known manner with use of the dispersion according to Preparation Example 2. The coating material of the invention could be adjusted without problems to the spray viscosity for the

application, without the occurrence of a phase separation hereby and/or precipitation of components. Multilayer coatings of excellent optical quality could be obtained with use of the basecoat–clearcoat method. This was still the case if the mixed coating composition (B) had been stored during the summer for several months at 30 to 40°C.

Aqueous Coating Material and Modular System for Producing Same

Claims

1. Aqueous coating material, prepared by combining

   (A) at least one base paint, containing

      (a1) at least one binder, optionally soluble or dispersible in water,
      (a2) at least one color- and/or effect-imparting pigment, and
      (a3) at least one water-miscible organic solvent, and if desired containing
      (a4) water,
      (a5) at least one crosslinking agent, and/or
      (a6) at least one auxiliary and/or additive;

   (B) at least one fine-particle solid mixed coating composition, containing

      (b1) at least one fine-particle solid binder, soluble or dispersible in water;

and

   (C) an aqueous medium.

2. Modular system for the preparation of aqueous coating materials, containing

   (I) at least one color and/or effect module, containing

      (A) at least one base paint, containing

         (al) at least one binder, optionally soluble or dispersible in water,
         (a2) at least one color- and/or effect-imparting pigment, and
         (a3) at least one water-miscible organic solvent, and if desired containing
         (a4) water,
         (a5) at least one crosslinking agent, and/or

(a6) at least one auxiliary and/or additive;

(II) at least one solids module, containing

(B) at least one fine-particle solid mixed coating composition, containing

(b1) at least one fine-particle solid binder, soluble or dispersible in water;

and

(III) at least one dispersion module, containing

(C) an aqueous medium.

3. Process for the preparation of an aqueous coating material by dispersion of

(A) at least one base paint, containing

(a1) at least one binder, optionally soluble or dispersible in water,
(a2) at least one color- and/or effect-imparting pigment, and
(a3) at least one water-miscible organic solvent,
and if desired containing
(a4) water,
(a5) at least one crosslinking agent, and/or
(a6) at least one auxiliary and/or additive;

and

(B) at least one mixed coating composition

in

(C) an aqueous medium,

characterized in that the mixed coating composition (B) is fine-particle and solid and contains

or consists of at least one fine-particle solid binder (b1).

4. The aqueous coating material according to claim 1, the modular system according to claim 2, and the process according to claim 3, characterized in that the component (B) contains

(b2) at least one color- and/or effect-imparting pigment,

(b3) at least one crosslinking agent, and/or

(b4) at least one auxiliary and/or additive.

5. The aqueous coating material according to claim 1 or 4, the modular system according to claim 2 or 4, and the process according to claim 3 or 4, characterized in that the binders (al) and (b1) are identical or different.

6. The aqueous coating material, the modular system, and the process according to claim 4 or 5, characterized in that the color- and/or effect-imparting pigments (a2) and (b2) are identical or different from each other.

7. The aqueous coating material, the modular system, and the process according to any one of claims 4 to 6, characterized in that the crosslinking agents (a5) and (b3) are identical or different from each other.

8. The aqueous coating material, the modular system, and the process according to any one of claims 4 to 7, characterized in that the auxiliaries and additives (a5) and (b4) are identical or different from each other.

9. The aqueous coating material according to any one of claims 1 or 4 to 8, the modular system according to any one of claims 2 or 4 to 8, and the process according to any one of claims 3 to 8, characterized in that fine-particle solid binder (b1) and if desired binder (al) contain either

(i) functional groups, which can be converted into cations by neutralizing agents and/or quaternization agents, and/or cationic groups, particularly sulfonium groups,

or

(ii) functional groups, which can be converted into anions by neutralizing agents, and/or anionic groups, particularly carboxylate groups and/or carboxylate groups,

and/or

(iii) nonionic hydrophilic groups, particularly poly(alkylene ether) groups.

10. The aqueous coating material, the modular system, and the process according to claim 10 [sic], characterized in that the fine-particle solid binder (b1) and optionally the binder (a1) contain carboxylic acid groups and/or carboxylate groups (ii).

11. Use of the aqueous coating materials according to any one of claims 1 or 4 to 10, the modular system according to any one of claims 2 or 4 to 10, or the process according to any one of claims 3 to 10 in production-line automotive finishing, refinishing, in particular, automotive refinishing, and the coating of plastics.

12. Production-line automotive finishing and refinishing paints and coatings of plastic, in particular topcoats and fillers for plastics, which can be prepared from aqueous coating materials according to any one of claims 1 or 4 to 10 and/or with the aid of the modular system according to any one of claims 2 or 4 to 10 and/or with the aid of the process according to any one of claims 2 to 11.

13. Objects, in particular automobiles, with production-line automotive finishing and refinishing paints, coatings for plastics, in particular topcoats and/or fillers for plastics, according to claim 12.